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(11) Publication number:

0 447 988 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **91104044.2**

(51) Int. Cl. 5: **B32B 27/08, B65D 65/40**

(22) Date of filing: **15.03.91**

(30) Priority: **23.03.90 IT 1978290**
05.09.90 IT 2138590

(43) Date of publication of application:
25.09.91 Bulletin 91/39

(54) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

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(54) **Multilayer thermosealing film for packaging.**

(37) A multilayer film for packaging comprising a thermosealing layer, a gas barrier layer and at least one additional polymeric layer, wherein the thermosealing layer comprises a copolymer selected from ethylene-methacrylic acid copolymers (EMAA) having a methacrylic acid (MAA) content of 4 to 18% by weight, ethylene-acrylic acid copolymers (EAA) having an acrylic acid content (AA) of 4 to 22% by weight, and their blends.

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This invention relates to the field of multilayer films for packaging, and more specifically to such films which are thermosealing, whether heat-shrinkable or not, as well as to container structures made from such films and to packages, particularly for food items, using such films and containers.

The use of multilayer films for packaging items in general, and foods in particular, is widespread nowadays. Depending on the performance to be achieved, the films comprise various plastic layers which, according to their chemical composition and the consequent properties, do perform the required function.

For the packaging of food items, the multilayer films usually comprise gas barrier layers for maintaining the package under vacuum or controlled atmosphere, structural layers which confer upon the films abuse and handling resistance, thermosealing layers for the cases when the hermetic sealing of the package is required, and possible bonding or adhesive layers interposed between the other layers for improving the cohesion of the multilayer film.

As thermosealing layers various polymeric materials have been used heretofore, amongst which the most widely used have been, for example, ethylene-vinyl acetate (EVA) copolymers, various ethylene polymers such as very low density linear polyethylene (LDPE), or ionomeric copolymers such as those available under the trademark Surllyn from E.I. Du Pont de Nemours and Inc. Co., (USA). These latter ionomeric polymers generally consist of copolymers of ethylene and methacrylic acid which are ionically cross-linked so as to convert them into metal salts, just designated as ionomers.

Notwithstanding the fact that such polymers used heretofore as thermosealing layers gave sufficiently satisfactory performance, they still had disadvantages which limited their use in certain applications. In particular, none of these polymers showed a sufficiently broad spectrum of properties comprising both a good sealability in the presence of contamination and of creases or folds in the sealing area as well as a good seal strength together with a wide sealing range in terms of temperature or time. From US 3,365,520 (DuPont), US 4,399,181 (Asahi-Dow) or US 4,414,053 (Gulf) films are known which comprise blends of ethylene-methacrylic acid (EMAA) with Surllyn, ethylene methyl acrylate (EMA) or other polymers, for use in forming oriented multilayer films. None of these prior patents discloses however an improved thermosealing layer as that which forms the subject-matter of this invention.

US Patent 4,879,124 discloses a cook-in perforated, gas permeable bag made of a multilayer film comprising a sealing layer and an additional layer of an EVA-LLDPE blend. The sealing layer, while generically hinted to as possibly comprising a polymer selected from EAA, EMAA and ionomers, is stated to be preferably made of a blend of 85% LLDPE with 15% ionomer or of such a blend in a 80/20 proportion.

According to this prior reference a bag is formed by providing a transverse sealing on a seamless perforated tubing length, then the bag is loaded with a food item, is closed by clipping or folding, is cooked and then it is finally placed in an additional, vacuum bag. Thus the sealing layer mentioned in this prior reference does not perform as a vacuum closure seal of a gas impermeable bag.

The main object of this invention is to provide a multilayer film comprising at least a thermosealing film and a gas barrier layer having an optimum combination of properties such as to render it suitable for use in packaging of various articles in various packaging and handling conditions.

More particularly, the object of this invention is to provide a multilayer film incorporating a gas barrier layer and a thermosealing layer having a good sealability in the presence of contamination or folds in the sealing area, an improved cold and hot seal strength, and a wide sealing range in terms of temperatures and times.

A further object of the invention is to provide packaging structures, like bags, etc. from the multilayer films of the invention, which are suitable both for cold packaging and for cooking-in the packaged food items.

These and other objects which will appear more clearly from the following disclosure are achieved by a multilayer thermoplastic film from which containers may be made, said film having a thermosealing layer, a gas barrier layer, and at least one additional polymeric layer characterized in that the thermosealing layer can be sealed to itself to form a container with an opening through which a product may be loaded into the container and after the container has been loaded, the film can be sealed to itself, through contaminants left by the product, to hermetically close the container, said thermosealing layer comprising a copolymer selected from ethylene-methacrylic acid (EMAA) copolymers with a methacrylic acid (MAA) content of about 4% to about 18% by weight, ethylene-acrylic acid (EAA) copolymers with an acrylic acid (AA) content of from about 4% to about 22% by weight, and their blends.

This invention is based on the discovery that an EMAA or EAA copolymer as defined above gives rise to a film for use as thermosealing layer, particularly in multilayer films, which has an excellent combination of properties.

Preferably, the thermosealing layer according to this invention comprises the said EMAA copolymer

with a MAA content of 9 to 15% by weight, e.g. of 12% by weight, or the said EAA copolymer with an AA content of 6 to 20% by weight or 12 to 18 % by weight, or a blend of such copolymers in any proportion.

According to further embodiments of the invention the thermosealing layer comprises a blend of 50 to 99% by weight of the EMAA copolymer as defined above, with 50 to 1% by weight of at least a further ethylene polymer or copolymer selected from linear low density polyethylene (LLDPE), linear very low density polyethylene (VLDPE), ethylene copolymers such as EBA (ethylene-butyl acrylate), EMA (ethylene-methyl acrylate), EVA (ethylene-vinyl acetate), and EVA modified with functional groups.

The multilayer film according to this invention comprises as said at least one additional polymeric layer a structural layer conferring upon the film mechanical or abuse resistance. Preferably the multilayer film of the invention comprises thus at least the following layers:

Sealing/ Barrier/ Structural

The gas barrier layer can be made of materials conventionally used for such purpose, for example of copolymers of vinylidene chloride with vinyl chloride or methyl acrylate or both, ethylene-vinyl alcohol (EVOH) copolymers, for example having an ethylene content of 30 to 47%, polyamides or copolyamides or blends thereof or with EVOH.

The structural layer which, beyond conferring abuse resistance, also increases the heat-shrink percentage when heat-shrinkable films are prepared, can be selected from polyethylenes of very low density (VLDPE), high density (HDPE), or linear low density (LLDPE); ethylene copolymers with vinyl or acrylic comonomers such as ethylene-vinyl acetate (EVA), ethylene-butyl acrylate (EBA), ethylene-methyl acrylate (EMA), ethylene-methacrylic acid (EMAA), ethylene-acrylic acid (EAA); ionomers; olefinic polymers and copolymers such as EVA, polyethylene (PE) or polypropylene (PP) modified with functional groups; polyamides such as Nylon 6, Nylon 6-66, Nylon 6-12, or Nylon 6-69; polyesters, copolyesters; and mixtures thereof.

As an ionomeric polymer Surllyn, for example, can be used.

Amongst the ethylene copolymers a preferred copolymer is EVA having a VA content of from 2 to 30% by weight, preferably of from 6 to 12% by weight.

Amongst the possible blends of the above polymers for producing the structural layer, blends of VLDPE and EVA in a weight ratio of 70:30 to 20:80 can be mentioned.

The multilayer film of the invention can comprise, in addition to the above-mentioned layers, further layers, such as adhesive layers, which improve the adhesion between the various functional layers. A structure of this type can comprise the following layers:

Sealing/ Adhesive/ Barrier/ Adhesive/ Structural

As adhesive layers, those commonly known for such use can be employed, e.g. EVA copolymers or PE or PP polymers modified with functional groups; linear low density polyethylene (LLDPE) or linear very low density polyethylene (VLDPE); copolymers selected from EVA, EBA, EMA, EMAA, EAA; ionomers; and mixtures thereof.

The EVA copolymers useful as adhesive have a VA content ranging from 6 to 25% by weight.

Preferably at least the thermosealing layer of a multilayer film according to the invention is cross-linked by electron beam irradiation at 1 to 15 MR. It has been found that such treatment notably increases the overall resistance of the obtainable seal, whether cold or hot.

According to a specific embodiment of this invention, the whole multilayer film can be irradiated to achieve cross-linking. In this case, the film can be prepared by simultaneous extrusion of all the layers, for example in tubular form, and their subsequent irradiation treatment.

According to an alternative embodiment, the multilayer film of the invention is produced by first coextruding a substrate comprising the EMAA or EAA thermosealing layer and possible further layers, in particular structural layers, then cross-linking the substrate by irradiation, and finally coextruding on the cross-linked substrate a coating comprising the further layers of the final film.

According to a still further embodiment of the invention, the multilayer film can be prepared by laminating various preformed films according to the desired structure, by using intermediate adhesive layers. The above mentioned adhesive materials can be used for this purpose. Also, in this embodiment part of the laminate or the whole laminate can be subjected to irradiation treatment.

Since for packaging food products it is advantageous to have heat-shrinkable films, the multilayer film of the invention is made heat-shrinkable by orientation through at least a mono-axial stretching in the longitudinal or transverse direction with respect to the direction of extrusion, but preferably through biaxial stretching, using techniques well-known in the field. For example, in the case when the film is prepared by coextrusion in tubular form, the bi-axial stretching can be performed by the "air-bubble" blowing method, on-line or off-line of the extrusion process. The multilayer film of this invention, either irradiated or not, has a thickness that depends on the number of layers, for example from 15 to 200 microns, preferably from 40 to

150 microns.

The following examples show, only for illustrative and not limitative purposes, various structures of multilayer films according to this invention.

5 Examples 1 to 10

The following films were prepared in accordance with this invention, each irradiated and non-irradiated version.

1. EMAA/ PVDC/ EMAA
- 10 2. EMAA/ PVDC/ EVA
3. EMAA/ PVDC/ 30 EVA + 70 LLDPE
4. EMAA/ EVOH/ EMAA
5. EMAA/ EVA/PVDC/ EVA
6. EMAA/ Adhesive 1/ PVDC/ Adhesive 1/ EMAA
- 15 7. EMAA/ EVA/ Adhesive 1/ PVDC/ VLDPE/ EVA
8. EMAA/ Adhesive 1/ PVDC/ Adhesive 1/ EVA
9. EMAA/ EVA/ Adhesive 1/ PVDC/ Adhesive 1/ Surlyn
10. EMAA/ EVA/ Adhesive 2/ EVOH/ Adhesive 2/ EVA

- The film of Ex. 10 which does not contain a PVDC layer has been prepared by simultaneously extruding
- 20 all the layers and irradiating then the entire coextrudate. It turned out to be suitable for cooking the packaged food product right in the package. Thus, this film has been used for packaging ham, and the so obtained package, after removal of air therefrom and its closure by sealing together two portions of the EMAA layer facing each other, has been cooked at 70-80° C whereby obtaining cooked ham.

25 Examples 11-17

The following film structures have been further prepared according to the invention, each in an irradiated and non-irradiated version.

11. EMAA/ EVA/ LLDPE/ EVA/ PVDC/ Adhesive 2/ Ny 6/12
- 30 12. EMAA/ B/ C
13. EMAA/ D/ Adhesive 2/ EVOH/ Adhesive 2/ D
14. EAA/ EVA/ PVDC/ EVA
15. EAA/ EVA/ EVA/ PVDC/ LLDPE/ EVA
16. EAA/ EVA/ EVA/PVDC/ EVA/ SURLYN
- 35 17. EAA/ EVA/ LLDPE/ EVA/ PVDC/ Adhesive 2/ NYLON

In the above examples 1 to 17 the abbreviations mean:

- | | |
|------------|--|
| EMAA | contains 12% MAA |
| EAA | contains 9% AA |
| EVA | contains 9% VA |
| 40 EVOH | contains 44% ethylene |
| Adhesive 1 | is an EVA copolymer containing 18% VA |
| Adhesive 2 | is an EVA copolymer modified by functional groups, available under the trademark Bynel from DuPont |
| Surlyn | is an ionomeric EMAA containing Na or Zn ions |
| 45 B | is a blend of 70/30 LLDPE/ EVA |
| C | is a blend of 30/70 LLDPE/ EVA |
| D | is a blend of 20/80 LLDPE/ EVA |

Example 18

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In order to evaluate the performance of a multilayer film according to this invention comparative tests have been run relating to the seal strength of such a film with respect to that of a conventional multilayer film which does not have an EMAA thermosealing layer.

The film of the invention had the following structure:

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4-ply EMAA/ EVA/ PVDC/ EVA

wherein the EMAA/EVA substrate has been cross-linked by irradiation, then extrusion coated with the remaining layers, and finally biaxially oriented. The EMAA sealing layer had an MAA content of 12%, while the EVA layer had a VA content of 9%.

The control film according to the prior art had the following structure:

4-ply Surlyn/ EVA/ PVDC/ EVA

wherein the Surlyn/EVA substrate had also been irradiated and then extrusion coated with the remaining layers.

- 5 The seal strength tests were run by measuring the burst resistance at room temperature (18-20 °C), and in hot by immersing the seal in a water bath at 85 °C. The results are given in the following table:

Table 1

10

Film	Seal strength	Hot seal strength
	at room temp. (inches water)	(mbar)
Ex. 18	190	95
Control	148	86

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25 From the above results it can be seen that the film according to the invention had a seal strength at room temperature which was notably improved, while the seal strength in hot was maintained at a level at least as good as that of the control film having a Surlyn thermosealing layer.

The multilayer films of the invention showed superior properties also with respect to other conventional materials used heretofore as thermosealing layers. Thus, they turned out to be superior to EVA copolymers as far as thermosealing in the presence of contamination is concerned, as for example that existing in the presence of meat products. Furthermore, the films of the invention showed themselves to be superior to VLDPE or LLDPE both with respect to sealability through folds and to the sealing range in terms of time and temperature: for example the films of this invention started to seal about 1/2 seconds before or at a temperature 10-20 °C below those used for VLDPE sealing layers.

30 The following example shows some comparative tests with respect to films having a LLDPE thermosealing layer.

35

Example 19

40 The film according to Ex.11 has been tested for seal strength and sealing range in comparison with a control film of the following structure:

Control: LLDPE/ EVA/ SURLYN/ EVA/ PVDC/ Adhesive 2/ Nylon 6-12

More specifically the sealing range and the seal strength have been determined both under clean conditions and in the presence of grease contamination at the sealing area, and the results are given in Figs. 1 and 2 of the enclosed drawings. Moreover, the quality of the seal made through folds has been evaluated by determining the reject percentage in vacuum packaging tests, wherein the packages which failed to maintain internal vacuum because of poor seals have been discarded. These latter results are plotted in the graph of Fig. 3.

45 From Figs. 1 and 2 it can be seen that the film of this invention starts to seal and achieves acceptable seal strength before the control film, a fact which translates in practice into energy savings and shortened production cycles.

From Fig. 3 it can also be noted that the reject percentage drops to zero for the film of this invention in much shorter times than for the control film, allowing thus for the same advantages of time and energy savings as mentioned above.

55 In addition to the multilayer films disclosed above, this invention also relates to containing structures formed therefrom, such as bags having a bottom seal or two lateral seals, formed at adjacent facing portions of the EMAA or EAA- based thermosealing layer.

Where technical features mentioned in any claim are followed by reference signs, those reference signs have been included for the sole purpose of increasing the intelligibility of the claims and accordingly, such

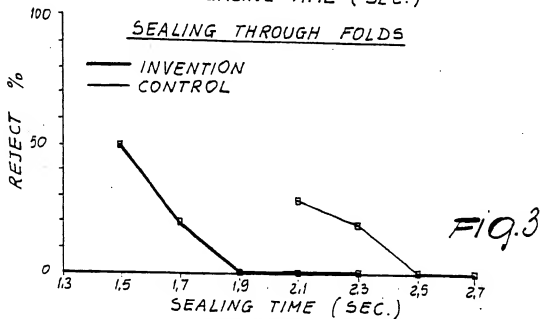
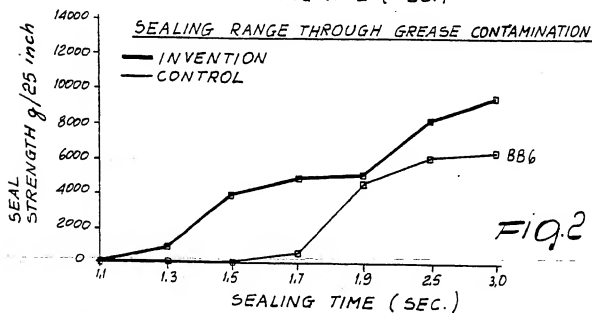
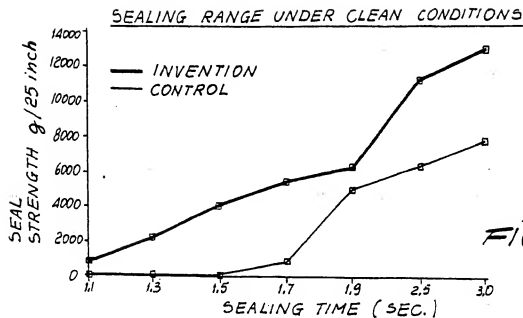
reference signs do not have any limiting affect on the scope of each element identified by way of example by such reference signs.

Claims

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1. A multilayer thermoplastic film from which containers may be made, said film having a thermosealing layer, a gas barrier layer, and at least one additional polymeric layer characterized in that the thermosealing layer can be sealed to itself to form a container with an opening through which a product may be loaded into the container and after the container has been loaded, the film can be sealed to itself through contaminants left by the product to hermetically close the container, said thermosealing layer comprising a copolymer selected from ethylene-methacrylic acid (EMAA) copolymers with a methacrylic acid (MAA) content of about 4% to about 18% by weight, ethylene acrylic acid (EAA) copolymers with an acrylic acid (AA) content of from about 4% to about 22% by weight, and their blends.
2. A film according to claim 1 wherein said EMAA copolymer has an MAA content of 9 to 15% by weight.
3. A film according to claim 1 wherein said EAA copolymer has an AA content of 6 to 20% by weight.
4. A film according to claim 1 wherein said thermosealing layer comprises a blend of 50 to 99% of said EMAA copolymer with 50 to 1% of said at least one further ethylene polymer or copolymer selected from ethylene-butyl acrylate (EBA), ethylene-methyl acrylate (EMA), VLDPE, LLDPE, ethylene-vinyl acetate (EVA) and EVA modified with functional groups.
5. A film according to claim 1 wherein the gas barrier layer is selected from copolymers of vinylidene chloride with vinyl chloride or methyl acrylate or mixtures of the two, ethylene-vinyl alcohol (EVOH) copolymers, polyamides or copolyamides or blends thereof with each other or with EVOH.
6. A film according to claim 1 wherein said additional polymeric layer is a structural layer selected from ethylene copolymers of very low density (VLDPE), high density (HDPE), or linear low density (LLDPE); ethylene copolymers with vinyl or acrylic comonomers; ionomers; olefinic polymers and copolymers modified with functional groups; polyamides; polyesters, copolyesters; and blends thereof.
7. A film according to claim 6 wherein said ethylene copolymers with vinyl or acrylic comonomers are selected from ethylene-vinyl acetate (EVA), ethylene-butyl acrylate (EBA), ethylene-methyl acrylate (EMA), ethylene-methacrylic acid (EMAA), ethylene-acrylic acid (EAA); said modified olefinic polymers and copolymers are selected from EVA, polyethylene and polypropylene modified with functional groups; and said polyamides are selected from Nylon 6, Nylon 6-66, Nylon 6-12 and Nylon 6-69.
8. A film according to claim 6 or 7 wherein said structural layer is selected from EVA copolymers with a VA content of 2 to 30%, VLDPE polymers, and blends of VLDPE and EVA in weight ratios of 70:30 to 20:80.
9. A film according to any one of the preceding claims wherein at least the thermosealing layer has been cross-linked by irradiation.
10. A film according to any one of the preceding claims which has been made thermoshrinkable by at least a monoaxial stretching.
11. A multilayer film according to claim 1 wherein the thermosealing layer consists essentially of EMAA copolymer having an MAA content of 4 to 18%.
12. The multilayer film of claim 1 wherein the thermosealing layer consists essentially of EMAA copolymer having a MAA content of 9 to 15%.
13. The multilayer film of claim 1 wherein the thermosealing layer consists essentially of EAA copolymer having AA content of 4 to 22% by weight.

14. Containing structure for packaging made of a multilayer film according to any one of claims 1 to 13 which is sealed together at two portions of said thermosealing layer arranged adjacent and facing each other.
- 5 15. Structure according to claim 14 in the form of a bag having a bottom seal.
16. Structure according to claim 14 in the form of a bag having two lateral seals.
- 10 17. A process for packaging food products such as fresh meat or poultry in thermoplastic vacuum bags made from seamless tubing wherein the tubing comprises at least three layers with the inner layer or wall being a thermosealing layer, and other layers being a gas barrier layer and an additional polymeric layer, characterized by the steps of: providing a thermosealing layer which comprises a copolymer selected from EMAA copolymers with a MAA content of 4 to 18% by weight, EAA copolymers with an
15 AA content of 4 to 22% by weight, and their blends; heat sealing the tubing transversely at spaced apart intervals to form the bottom seal for a bag and severing the tubing to provide an opening or mouth for the thus formed bag; filling the bag with a food product; and, thereafter, evacuating and transversely heat sealing the bag through any contaminants left by the food product to hermetically seal same.
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 224 862 (WOLFF WALSRODE AG) * page 2, lines 14 - 24 ** page 4, line 28 - page 5, line 8 ** page 5, lines 13 - 16 ** page 5, lines 28 - 36 @ page 8, lines 17 - 21 ** page 8, lines 30 - 35 ** page 11, lines 6 - 16 * - - -	1-17	B 32 B 27/08 B 65 D 65/40
Y	US-A-4 820 557 (WARREN) * column 2, lines 37 - 47 ** column 5, lines 57 - 68 @ column 6, lines 42 - 52 @ column 8, lines 33 - 66 @ claims 4-14 * - - -	1-3,5-17	
Y	US-A-4 678 836 (MCKINNEY ET AL.) * column 2, lines 5 - 9 ** column 11, lines 20 - 31; claim 1 * - - -	4	
A	US-A-4 228 215 (HEIN, III ET AL.) * column 2, line 67 - column 3, line 16 ** column 3, line 64 - column 4, line 45 ** column 5, lines 16 - 40 ** column 6, lines 37 - 57 * - - -	1-17	
A	FR-A-2 445 212 (W. R. GRACE & CO.) * page 1, lines 1 - 12 ** page 3, lines 18 - 33 @ page 4, lines 28 - 31 @ page 6, lines 3 - 22 @ page 8, lines 10 - 11 @ page 8, lines 16 - 19 ** page 11, lines 7 - 20; claims 8, 9 * - - -	1-13	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	US-A-4 755 402 (OBERLE) * column 2, lines 58 - 62 ** column 3, lines 26 - 31 @ column 4, lines 14 - 21 @ column 5, lines 26 - 37 @ column 6, line 66 - column 7, line 15 ** column 7, lines 36 - 45; claims 1, 4-6 * - - -	1-17	B 32 B C 08 L 23
A	EP-A-0 001 898 (MOBIL OIL CORP.) * page 3, lines 11 - 17 ** page 4, lines 7 - 20 ** page 5, lines 29 - 36; claims 1, 3 * - - -	1-3	
The present search report has been drawn up for all claims		-/-	
Place of search		Date of completion of search	Examiner
The Hague		02 July 91	IBARROLA TORRES O.M.
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention			
E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document			



EUROPEAN SEARCH
REPORT

EP 91 10 4044

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 351 931 (ARMITAGE) * column 9, lines 7 - 16; claims 1-11 * -----	1-3	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 02 July 91	Examiner IBARROLA TORRES O.M.
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention		E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document	